

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-297105

(43) 公開日 平成9年(1997)11月18日

(51) Int.Cl. <sup>9</sup>	識別記号	庁内整理番号	F I	技術表示箇所
G 0 1 N 21/78			G 0 1 N 21/78	C
C 0 1 C 3/00			C 0 1 C 3/00	Z
G 0 1 N 31/00			G 0 1 N 31/00	R
35/08			35/08	D

審査請求 未請求 請求項の数 2 O L (全 6 頁)

(21) 出願番号 特願平8-111409

(22) 出願日 平成8年(1996)5月2日

特許法第30条第1項適用申請有り 平成8年3月13日  
 社団法人日本化学会発行の「日本化学会第70春季年会講  
 演予稿集▲I▼」に発表

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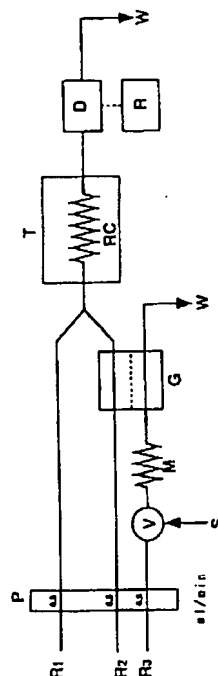
(54) 【発明の名称】 シアンの高感度検出法及びそのための装置

(57) 【要約】

【課題】 シアンの高感度検出法及び装置を提供する。

【解決手段】 フローインジェクションアナリシスシステムに気体拡散ユニットを組み込み、サンプル溶液由来のシアン化水素をオルトフタルアルデヒド溶液に吸収させ、この溶液と第1級アンモニウム又はアミン溶液と反応させてイソインドール誘導体を縮合形成し、この誘導体に紫外線を照射して生じる蛍光の大きさを測定してシアンの定量を行う。

【効果】 特異性 (シアン選択性) に優れ、測定所要時間が短く (2分間程度) 且つ極めて高感度 (ng/ml 即ち ppb のオーダーで測定可能) である。



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## 【特許請求の範囲】

【請求項1】 フローインジェクションアナリシスであって、サンプル溶液中のシアン化合物を気体化させてオルトフタルアルデヒド溶液に吸収させ、この溶液と第1級アンモニウム又は第1級アミン溶液とを混合し恒温槽に導いて上記オルトフタルアルデヒドと、シアン化合物と、第1級アンモニウム又は第1級アミンとを縮合させてイソインドール誘導体を形成し、該誘導体に紫外線を照射して蛍光の大きさを測定することを特徴とする、シアンの高感度検出法。

【請求項2】 第1級アンモニウム又は第1級アミン溶液と、オルトフタルアルデヒド溶液と、緩衝液とを同時に且つ別途に送液する多チャンネルポンプと、上記緩衝液の流路に設けられたサンプルインジェクターと、上記オルトフタルアルデヒド溶液と緩衝液の両流路に亘って設けられていてサンプル溶液中のシアン化合物を気体としてオルトフタルアルデヒド溶液に吸収させる気体透過性ユニットと、恒温槽と、該恒温槽内に配設されていてシアン化合物含有オルトフタルアルデヒド溶液と第1級アンモニウム又は第1級アミン溶液の混合物を反応させるコイルと、反応生成物に紫外線を照射することにより発生する蛍光を検出する蛍光検出器とを具備していることを特徴とする、シアンの高感度検出装置。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明はシアンの検出法及びそのための装置に係り、殊にフローインジェクションアナリシス（以下「FIA」と略記する場合がある）システムに気体拡散ユニットを組込むと共に、サンプル中のシアン化合物をイソインドール誘導体に導いて蛍光の大きさを測定する、シアンの高感度検出法及びそのための装置に係る。

## 【0002】

【従来の技術】河川水等の水域環境への毒物の混入は、富栄養化と並んで極めて深刻な問題である。殊に、シアンは猛毒であって生物の呼吸活性を阻害するため、その濃度によっては生物が死に至る危険性もある。シアンはメッキ工場等で頻繁に使用されており、その工場排水中への混入、更には水域環境への混入は極めて危険であり、高感度で迅速な検出及びその測定装置の開発が切望されている。

【0003】従来におけるシアンの標準的な検出法として日本工業規格（JIS）にはビリジーン-ピラゾロン法が規定されている。一般に、サンプル溶液中において、シアンはシアンイオン（ $CN^-$ ）や安定度の異なる種々のシアン錯体の形で存在しているので、JIS法においてはサンプル溶液に前処理が、先ず、施される。この前処理とはシアン化合物を pH の違いにより段階的に捕集するものである。即ち、サンプル溶液の pH を 5.5、5.0 及び 2 以下に調節した後、pH 5.0 の場合には 40℃ に加温

し通気することにより、又 pH 5.5 及び 2 以下の場合には加熱蒸留することによりシアン化水素を発生させ、これをそれぞれ水酸化ナトリウム水溶液により捕集するのである（この場合に特に、pH 2.0 以下で発生するシアン水素は「全シアン」と称される）。上記のようにして得られた、シアン化水素含有水酸化ナトリウム水溶液（以下、「検査溶液」と称する）が下記の要領による測定に供される。

ビリジーン-ピラゾロン法：酢酸と、磷酸ナトリウム-磷酸カリウム緩衝液と、クロラミン T と、発色試薬としての 1-フェニル-3-メチル-5-ピラゾロンとビス(1-フェニル-3-メチル-5-ピラゾロンとの混合溶液を一定量の検査溶液に添加し、波長 620nm 付近で吸光度を測定して定量する。

4-ビリジンカルボン酸-ピラゾロン法：前者とはほぼ同様であるが、発色試薬として 4-ビリジンカルボン酸-ピラゾロン溶液（1-フェニル-3-メチル-5-ピラゾロンの N,N-ジメチルホルムアミド溶液と 4-ビリジンカルボン酸水溶液との混合溶液）を使用し、これをビリジーン-ピラゾロン法に関して述べた他の試薬と混合し、この混合溶液を一定量の検査溶液に添加し、波長 620nm 付近で吸光度を測定して定量する。上記の測定法の他に、シアン選択性電極を用いる方法及びイオンクロマトグラフィーを利用する方法がシアン化合物の検出法として用いられている。これらの両方法の内でシアン選択性電極を用いる方法においては電極先端の AgS とシアンとの反応を電圧変化により検出する。

## 【0004】

【発明が解決しようとする課題及び発明の目的】シアン検出の従来法として上記の諸方法を挙げることができるが、ビリジーン-ピラゾロン法や 4-ビリジンカルボン酸-ピラゾロン法は前処理が煩雑であり且つ前処理後の測定自体にも時間を要する点に課題がある。このために、河川等の水域環境に関するシアンの連続測定にはシアンイオン選択性電極を用いる方法が利用されてきた。しかしながら、この方法はサンプル溶液中に沃化物や硫化物が存在すると干渉を受け易い点に課題がある。一方、イオンクロマトグラフィーを利用する方法は、高価で大型の機器を必要とするために、様々な場所において河川水等の連続的な定点測定を行う関係上、コスト的に適さない。

【0005】従って、本発明の目的は迅速、簡便且つ極めて高感度であり、シアンに対して選択性が高く、実際にも利用可能なシアン検出法を確立し且つそのための装置を提供することにある。

## 【0006】

【課題を解決するための手段】本発明によれば、フローインジェクションアナリシスであって、サンプル溶液中のシアン化合物を気体化させてオルトフタルアルデヒド（以下「OPA」と略記する場合がある）溶液に吸収さ

せ、この溶液と第1級アンモニウム又は第1級アミン溶液とを混合し恒温槽に導いて上記オルトフタルアルデヒドと、シアン化合物と、第1級アンモニウム又は第1級アミンとを縮合させてイソインドール誘導体を形成し、該誘導体に紫外線を照射して蛍光の大きさを測定することを特徴とするシアンの高感度検出法により既述の課題が解決されると共に、上記の目的が達成される。

【0007】一方、上記の方法を実施するための本発明装置は第1級アンモニウム又は第1級アミン溶液と、オルトフタルアルデヒド溶液と、緩衝液とを同時に且つ別途に送液する多チャンネルポンプと、上記緩衝液の流路に設けられたサンプルインジェクターと、上記オルトフタルアルデヒド溶液と緩衝液の両流路に亘って設けられていてサンプル溶液中のシアン化合物を気体としてオルトフタルアルデヒド溶液に吸収させる気体透過性ユニットと、恒温槽と、該恒温槽内に配設されていてシアン化合物含有オルトフタルアルデヒド溶液と第1級アンモニウム又は第1級アミン溶液の混合物を反応させるコイルと、反応生成物に紫外線を照射することにより発生する蛍光を検出する蛍光検出器とを具備していることを特徴としている。

【0008】本発明において気体拡散法が採択された理由は、シアン化合物と同様にチオール類や亜硫酸も縮合反応し、これらの縮合生成物に紫外線を照射すれば蛍光を発することが知られており、実際の河川水等には種々の物質が溶存していることを勘案し、シアン検出の選択

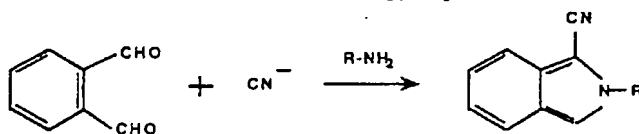
\*性乃至特異性の向上を図るためである。この気体拡散法とは、検査溶液中に初めから存在した気体或いは分析システム内で化学反応によって生成した気体を他の液相へ拡散させるもので、一般に、相分離は適当な膜を利用して行われる。この分離の目的は複雑な検査溶液中の妨害物質を除去することであり、従って測定目的物質の選択性と感度を向上させることができる。

【0009】本発明方法において採用されているFIAとは、細管中を流れるキャリアー溶液の中にサンプル溶液を直接注入してサンプルからの信号を検出する方法であり、システムの製作が簡単であるだけでなく、迅速に目的物質の連続的測定が可能と云う利点を有している。又、流れの中でのサンプルと試薬の混合は主に拡散律速で起こり、蛍光反応のような瞬間的な反応も検出可能である。更にこの連続的な流れの中でサンプルと試薬の混合が正確にコントロールされるためにFIAによる測定の精度は測定誤差が1%以内ときわめて高いものであることが期待できる。従ってフロー型検出装置を構築する場合にFIAは極めて有効な手段である。

【0010】本発明方法において採用されている縮合はOPAと、シアン化合物と、第1級アンモニウム又は第1級アミンとを反応させてイソインドール誘導体に導くものであり、第1級アミンを用いた場合について反応式にて示せば下記の通りである。

【0011】

【化1】



【0012】本発明方法においては、上記の縮合生成物が蛍光反応に供される。この蛍光反応とは紫外線等の光エネルギーを与えることにより基底状態にあった電子が不安定な励起状態になり、この状態から元の安定した基底状態に戻る際に、励起状態の時に吸収したエネルギーを光として放出する現象を指称する。この反応を用いた蛍光光度法は従来用いられてきた吸光光度法に比べて感度及び選択性の両者において優れており、自然蛍光物質の分析のみならず、蛍光誘導体化を行うことにより、蛍光性を本来有していない物質にも適用できると云う利点を有している。この場合に生じる蛍光の大きさは蛍光検出器で測定され、次いで積算計で記録され、検出面積として表わすことができる。

【0013】本発明方法を実施する場合に、サンプル溶液中のシアン化合物は気体拡散によりシアン化水素の形で選択的に蛍光検出流路側に供給される。サンプル溶液中に高濃度のシアン化合物が含まれている場合は、これに比例して高濃度のシアン化水素が分離されるために高い応答値が得られる。即ち、サンプル溶液中のシアン濃

度に依存して蛍光検出によって得られる応答値も高くなり、シアン濃度と応答値は比例する。従ってシアン濃度に対する応答値の検量線が得られ、未知濃度のサンプル溶液中のシアン濃度測定が可能である。

【0014】次に、図面を参照しつつ、本発明によるシアン検出装置及び操作方法並びに測定試験例について説明する。

【実施例】図1には本発明によるシアン検出装置の1実施形が略示されている。この図1において、R1は2.0mM グリシン溶液(第1級アンモニウムとして採択)の導入部であり、R2は0.2mM OPA溶液と0.1M 磷酸緩衝液との混合液の導入部であり、R3は0.1M 磷酸緩衝液の導入部であり、Pは蠕動性ポンプであり、Sはサンプル溶液の導入部であり、Vはサンプルインジェクターであり、Mは混合コイルであり、Gは気体透過性ユニットであり、Tは恒温槽であり、RCは反応コイルであり、Dは蛍光検出器であり、Rは積算記録計であり、Wは廃液である。このシアン検出装置において、蠕動性ポンプPとしては4チャンネルの各流路に対して同時に



化カリウム濃度と検出面積との関係を示す図である。

【符号の説明】

R1 : グリシン溶液 (第 1 級アンモニウム溶液)

R2 : OPA 溶液と磷酸緩衝液との混合液

R3 : 磷酸緩衝液

P : 蠕動性ポンプ

S : サンプル溶液

V : サンプルインジェクター

\* M : 混合コイル

G : 気体透過性ユニット

T : 恒温槽

RC : 反応コイル

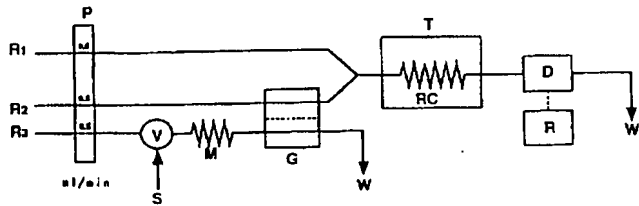
D : 蛍光検出器

R : 積算記録計

W : 廃液

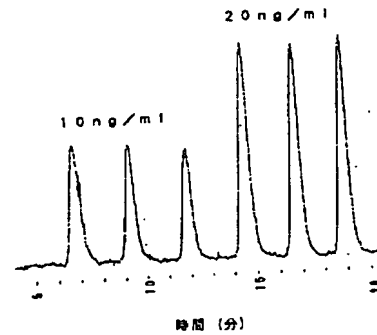
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【図 1】

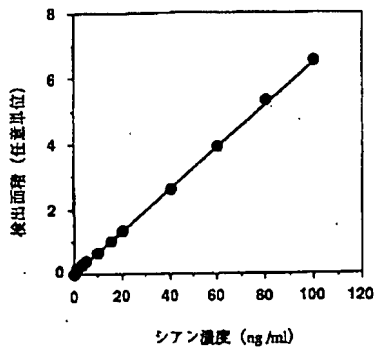


R1 : グリシン溶液 (第 1 級アンモニウム溶液)  
R2 : OPA 溶液と磷酸緩衝液との混合液  
R3 : 磷酸緩衝液  
P : 蠕動性ポンプ  
S : サンプル溶液  
V : サンプルインジェクター  
M : 混合コイル  
G : 気体透過性ユニット  
T : 恒温槽  
RC : 反応コイル  
D : 蛍光検出器  
R : 積算記録計  
W : 廃液

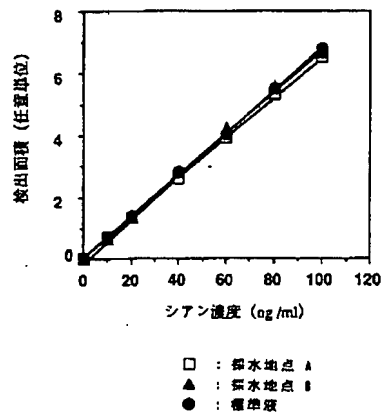
【図 2】



【図 3】



【図 4】



フロントページの続き

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# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-297105

(43)Date of publication of application : 18.11.1997

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(51)Int.Cl. G01N 21/78

C01C 3/00

G01N 31/00

G01N 35/08

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(21)Application number : 08-111409

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(22)Date of filing : 02.05.1996

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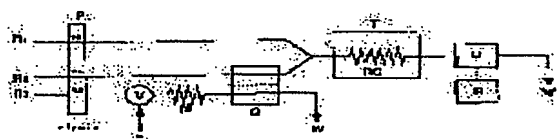
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(54) METHOD OF DETECTING CYAN WITH HIGH SENSITIVITY, AND DEVICE THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance the sensitivity of detection by evaporating a cyan compound, absorbing it to an OPA (orthophthalaldehyde) solution, condensing the OPA, the cyan compound, and primary ammonium to form an isoindole derivative, and emitting an ultraviolet ray thereto to measure the magnitude of fluorescence.

SOLUTION: A sample solution S injected through an injector V is mixed with a phosphoric acid buffer solution R3 and guided to a gas diffusing unit G. The cyan compound within the sample is



absorbed by a mixture of OPA which is a receiving solution and a sodium borate buffer solution in the form of hydrogen cyanide through a gas permeable membrane. The receiving solution having the hydrogen cyanide absorbed therein is mixed with a glycine solution (primary ammonium solution) R1. A reacting coil RC is heat-insulated within a thermostatic chamber T, in which the OPA, hydrogen cyanide and glycine are condensed to form an isoindole derivative. An ultraviolet ray is emitted thereto, and the generated fluorescence is detected by a fluorescent detector D.



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## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]



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**CLAIMS**

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[Claim(s)]

[Claim 1] Are a flow injection analysis, and make the cyanides in a sample solution gasificate and an alt.phthalaldehyde solution is made to absorb. This solution and \*\* 1 Class ammonium or \*\* 1 A class amine solution is mixed and it leads to a thermostat. The above-mentioned alt.phthalaldehyde, Cyanides and \*\* 1 Class ammonium or \*\* The high sensitivity detecting method of cyanogen which is made to carry out condensation of the 1st class amine, and is characterized by forming iso indole derivatives, irradiating ultraviolet rays at this derivative, and measuring the magnitude of fluorescence.

[Claim 2] \*\* 1 Class ammonium or \*\* 1 A class amine solution and an alt.phthalaldehyde solution, To coincidence the buffer solution And the multi-channel pump which sends the liquid separately and the sample injector formed in the passage of the above-mentioned buffer solution, The permeability unit which it is continued and prepared in both the passage of the above-mentioned alt.phthalaldehyde solution and the buffer solution, and an alt.phthalaldehyde solution is made to absorb by making the cyanides in a sample solution into a gas, It is arranged in the thermostat and this thermostat and they are a cyanides content alt.phthalaldehyde solution and \*\*. 1 Class ammonium or \*\* 1 The coil to which the mixture of a class amine solution is made to react, High sensitivity detection equipment of cyanogen characterized by providing the fluorescence detector which detects the fluorescence generated by irradiating ultraviolet rays at a resultant.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] The method of detecting cyanogen and the equipment for it are started, and this invention is a flow injection analysis especially. (it may be written as "FIA" below) While including a gaseous diffusion unit in a system, the high sensitivity detecting method of cyanogen which leads the cyanides in a sample to iso indole derivatives, and measures the magnitude of fluorescence, and the equipment for it are started.

[0002]

[Description of the Prior Art] Mixing of the poison to water area environments, such as river water, is a very serious problem together with eutrophication. Especially, cyanogen is a deadly poison, and it has the danger that a living thing will die depending on the concentration in order to check the respiratory activity of a living thing. Cyanogen is used frequently at plating works etc. and it is anxious for mixing through which it passes among the industrial liquid waste, and the development which mixing to a water area environment is very more dangerous still, and is quick detection and its measuring device in high sensitivity.

[0003] as the standard method of detecting the cyanogen in the former — Japanese Industrial Standards (JIS) \*\*\*\* — the pyridine-pyrazolone method is specified. Generally, it sets in a sample solution and cyanogen is cyanide ion. (CN<sup>-</sup>) Since it exists in the form of various cyanogen complexes where stability differs, it is JIS. In law, pretreatment is first performed to a sample solution. This pretreatment is cyanides. pH Uptake is gradually carried out by difference. Namely, sample solution pH 5.5 5.0 It reaches. 2 pH 5.0 after adjusting below In the case 40 degrees C By warming and carrying out aeration moreover — pH 5.5 and — 2 By carrying out heating distillation in the following cases, a hydrogen cyanide is generated and uptake of this is carried out with a sodium-hydroxide water solution, respectively. (in this case — especially — pH 2.0 — the cyanogen hydrogen generated below is called a "total cyanide") . Hydrogen-cyanide content sodium-hydroxide water solution obtained as mentioned above (an "inspection solution" is called hereafter) Measurement by the following point is presented.

Pyridine-pyrazolone method 1-phenyl-3-methyl-5-pyrazolone and screw : an acetic acid, the sodium phosphate-potassium phosphate buffer solution, and chloramine (a mixed solution with 1-phenyl-3-methyl-5-pyrazolone is added in the inspection solution of a

constant rate, and it is wavelength [ The quantum of the 620nm of the absorbances is measured and carried out near. ]) T As a color reagent

The 4-pyridinecarboxylic acid-pyrazolone method : Although it is the same as that of the former almost, it is a color reagent. 4-pyridinecarboxylic acid-pyrazolone solution (mixed solution of N.N-dimethylformamide solution of 1-phenyl-3-methyl-5-pyrazolone, and a 4-pyridinecarboxylic acid water solution) It is used, and mixes with other reagents which described this about the pyridine-pyrazolone method, this mixed solution is added in the inspection solution of a constant rate, and it is wavelength. 620nm The quantum of the absorbance is measured and carried out near. The method of using the approach and ion chromatography which use the cyanogen selectivity electrode other than the above-mentioned measuring method is used as a method of detecting cyanides. It sets to the approach using a cyanogen selectivity electrode among [ it is both a method ] these, and is an electrode tip. AgS Electrical-potential-difference change detects a reaction with cyanogen.

[0004]

[Object of the Invention and the purpose of invention] Although many above-mentioned approaches can be mentioned as a conventional method of cyanogen detection, it is a pyridine-pyrazolone method. The 4-pyridinecarboxylic acid-pyrazolone method has complicated pretreatment, and a technical problem is in the point that the measurement after pretreatment itself takes time amount. For this reason, the method of using a cyanide ion selectivity electrode is used for the continuous measurement of the cyanogen about water area environments, such as a river. However, this approach has a technical problem in the point of being easy to receive interference, when an iodide and a sulfide exist in a sample solution. locations various on the other hand, since the method of using ion chromatography needs an expensive and large-sized device — setting — the continuous fixed points, such as river water, — it is not suitable in cost on the relation which measures.

[0005] therefore, the purpose of this invention — quickness — it is high sensitivity very much and is in simple and selectivity being high, and establishing the available cyanogen detecting method also in fact to cyanogen, and offering the equipment for it.

[0006]

[Means for Solving the Problem] According to this invention, are a flow injection analysis, the cyanides in a sample solution is made to gasificate, and it is an alt.phthalaldehyde. (it may be written as "OPA" below) A solution is made to absorb. This solution and \*\* 1 Class ammonium or \*\* 1 A class amine solution is mixed and it leads to a thermostat. The above-mentioned alt.phthalaldehyde, Cyanides and \*\* 1 Class ammonium or \*\* 1 Carry out condensation of the class amine and iso indole derivatives are formed. While a technical problem as stated above is solved by the high sensitivity detecting method of the cyanogen characterized by irradiating ultraviolet rays at this derivative and measuring the magnitude of fluorescence, the above-mentioned purpose is attained.

[0007] On the other hand, this invention equipment for enforcing the above-mentioned approach is \*\*. 1 Class ammonium or the 1st Class amine solution, To coincidence an alt.phthalaldehyde solution and the buffer solution And the multi-channel pump which sends the liquid separately, The sample injector formed in the passage of the above-mentioned buffer solution, the permeability unit which it is continued and prepared in both the passage of the above-mentioned alt.phthalaldehyde solution and the buffer

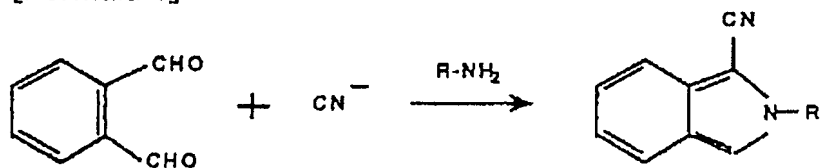
solution, and an alt.phthalaldehyde solution is made to absorb by making the cyanides in a sample solution into a gas, and a thermostat, It is arranged in this thermostat and they are a cyanides content alt.phthalaldehyde solution and \*\*. 1 Class ammonium or the 1st The coil to which the mixture of a class amine solution is made to react, It is characterized by providing the fluorescence detector which detects the fluorescence generated by irradiating ultraviolet rays at a resultant. <BR> [0008] The reason the gaseous diffusion method was adopted in this invention is for knowing emitting fluorescence, if the condensation reaction also of thiols or the sulfurous acid is carried out and they irradiate ultraviolet rays at these condensation products, taking into consideration that various matter is dissolved in actual river water, and aiming at improvement in the selectivity of cyanogen detection thru/or singularity. [ as well as cyanides ] This gaseous diffusion method diffuses the gas generated by the chemical reaction within the gas which existed from the start in the inspection solution, or the analysis system to other liquid phase, and, generally phase separation is performed using the suitable film. The purpose of this separation is to remove the interfering substance in a complicated inspection solution, therefore can raise the selectivity and sensibility of the quality of the measurement specified substance.

[0009] It is adopted in this invention approach. FIA It is the approach of pouring in a sample solution directly into the carrier solution which flows the inside of a capillary, and detecting the signal from a sample, and has the advantage which manufacture of a system is not only easy, but says that continuous measurement of the quality of the specified substance is quickly possible. Moreover, the sample in the inside of flow and mixing of a reagent mainly take place by the diffusion limitation, and can also detect a momentary reaction like a fluorescent reaction. Furthermore, since mixing of a sample and a reagent is correctly controlled in this continuous flow A measurement error the measuring accuracy by FIA 1% It is less than expectable that it is very high. Therefore, when flow mold detection equipment is built FIA It is a very effective means.

[0010] Condensation adopted in this invention approach OPA Cyanides and \*\*. 1 Class ammonia or \*\*. 1 A class amine is made to react, and it leads to iso indole derivatives, and is \*\*. 1 It will be as follows if a reaction formula shows the case where a class amine is used.

[0011]

[Formula 1]



[0012] A fluorescent reaction is presented with the above-mentioned condensation product in this invention approach. It will be in an excitation state with the unstable electron which suited the ground state by giving light energies, such as ultraviolet rays, with this fluorescent reaction, and in case it returns from this condition to the ground state by which origin was stabilized, the designation of the phenomenon which emits as a light the energy absorbed at the time of an excitation state is carried out. The fluorography using this reaction is excellent in both sensibility and selectivity compared with the absorptiometry used conventionally, and has the advantage referred to as

applicable not only to analysis of the native fluorescence matter but the matter which originally does not have fluorescence by performing fluorescence derivatization. In this case, the magnitude of the fluorescence to produce is measured with a fluorescence detector, subsequently is recorded with an integrator, and can be expressed as a detection area.

[0013] When enforcing this invention approach, the cyanides in a sample solution is alternatively supplied to a fluorescence detection passage side by gaseous diffusion in the form of a hydrogen cyanide. When high-concentration cyanides is contained in the sample solution, since a high-concentration hydrogen cyanide is separated in proportion to this, a high response value is acquired. That is, the response value acquired by fluorescence detection depending on the cyanogen concentration in a sample solution also becomes high, and cyanogen concentration is proportional to a response value. Therefore, the calibration curve of the response value over cyanogen concentration is acquired, and the cyanogen density measurement in the sample solution of strange concentration is possible.

[0014] Next, the example of a measurement trial is explained to the cyanogen detection equipment and the operating-instructions list by this invention, referring to a drawing.

[Example] drawing 1 \*\*\*\* — cyanogen detection equipment by this invention 1 It sketches the operation form. This drawing 1 It sets and is R1. 2.0mM Glycine solution (\*\* 1 it adopts as class ammonium) It is induction. R2 0.2mM OPA Solution 0.1M It is the induction of mixed liquor with a phosphate buffer. R3 0.1M It is the induction of a phosphate buffer and is P. It is a peristalsis nature pump. S It is the induction of a sample solution and is V. It is a sample injector and is M. It is a mixed coil and is G. It is a permeability unit and is T. It is a thermostat and RC. It is a reaction coil and is D. It is a fluorescence detector and R. It is an addition recorder and is W. It is waste fluid. It sets to this cyanogen detection equipment, and is a peristalsis nature pump. P If it carries out 4 The liquid can be sent to coincidence to each passage of a channel. GILSON Shrine make MINIPULS 3 It is used. Gaseous diffusion unit G If it carries out Tecator Shrine make 5000-3760 CHEMIFOLD EXTTYPE V It is used. As gas transparency film with which this gaseous diffusion unit is equipped, it is company make. Gasdiffusion Membrane 5000-2875 It was used. To this gaseous diffusion unit, the above-mentioned gas permeable membrane made from Teflon is separated, a shallow slot is in both sides, and it is made as [ flow / supply liquid and acceptance liquid ]. The hydrogen-cyanide gas which occurred from the sample moves to an acceptance liquid flow from a supply liquid flow through the gas transparency film. In this example, it is supply liquid. 0.1M (pH 7.0) A phosphate buffer is used and it is acceptance liquid. 0.2mM OPA It contains. 0.1M Sodium borate buffer solution (pH 9.5) It was used. as the tube for liquid sending of a system — the pump section — bore 1.15mm a fur — a prospect — tube (NORTON shrine make) the thermostat section — bore 0.05mm the parts of a stainless steel tube and others — bore The 0.5mm peak tube was used. As a sample injector, it is an injector for high speed liquid chromatographies. (REODYNE shrine make and 7125 mold) It reaches. 100microl The sample loop formation was used.

[0015] Detection of the cyanogen using above equipment is performed in the following way. Injector (V) The sample solution passed through and poured in is 0.1M (pH 7.0) which are carrier liquid. Phosphate buffer (R3) It is mixed and is a gaseous diffusion unit. (G) It is led and the cyanides in a sample is acceptance liquid in the form of a hydrogen

cyanide here. It is absorbed by the mixed liquor of OPA and boric acid acid sodium buffer-solution (pH 9.5) through the gas transparency film. Acceptance liquid which absorbed the hydrogen cyanide in this way 2.0mM Glycine solution (R1) It is mixed. Reaction coil (RC) For example 50-degree C thermostat (T) It is kept warm inside and is here. The condensation of OPA, a hydrogen cyanide, and a glycine arises, and iso indole derivatives are formed. this condensation product — ultraviolet rays (excitation wavelength 328nm) the fluorescence irradiated and produced — spectrophotometer [— made in Hitachi, Intelligent Spectrofluorometer 821-FP, and measurement wavelength 370nm] the peak area detect and corresponding to concentration — integrator [Made in Hitachi and Chromato-Integrator D-2500] It records.

[0016] Example of a measurement trial 1 concentration 10 ng/ml It reaches. 20 ng/ml A potassium-cyanide water solution is prepared and it is drawing. 1 The result of having poured into the equipment shown as a sample solution, having made carrying out a condensation reaction to other reagents, having measured the fluorescence which irradiates ultraviolet rays and is generated in a resultant, and having investigated the detection peak is drawing. 2 It is shown. It became clear from this drawing that responsibility also becomes high depending on the amount of cyanides. this drawing — setting — elapsed time 20 a part — between — although it had become, since this poured the sample solution into equipment intermittently — it is — the actual measuring time — the time amount from the origin of a peak to a terminal point — it is — therefore — 2 a part — between — extent — it was very short, and in the case of the sample solution of the same concentration, since the peak height was identical mostly, it became clear that repeatability is also high. Example of a measurement trial 2 [0017]

Concentration Zero to 100 ng/ml A potassium-cyanide water solution is prepared and it is drawing. 1 The result of having poured into the equipment shown as a sample solution, having made carrying out a condensation reaction to other reagents, having measured the fluorescence which irradiates ultraviolet rays and is generated in a resultant, and having investigated the relation between potassium-cyanide concentration and detection area is drawing. 3 It is shown. this drawing to potassium-cyanide concentration One to 100 ng/ml linearity obtains in between — having — minimum-limit-of-detection concentration 1 ng/ml it is — things became clear.

[0018] example of a measurement trial being possible in compaction of the fast measuring time as compared with the conventional technique, as long as the cyanides content water solution prepared as a sample is used for the cyanogen detecting method by this invention from the result shown in the example of a trial of 3 above — carrying out — further — The thing with possible and high sensitivity measurement of ng/ml (ppb) order repeatability is [ the thing ] high became clear. Therefore, in order to verify the practicality of this invention, river water is extracted in a different location. Near [ [\*\*\*\*\*] ] (bottling-water point A), BOD 1.04 and pH 7.9 And near the Kawashima pons (bottling-water point B) After BOD 2.83, pH 7.5, and all check with a conventional method that reservoirs-along-the-Tone-River] and these river water do not contain cyanides To these river water and distilled water Zero to 100 ng/ml A potassium cyanide is added by concentration. It is drawing 1, using these as a sample solution. It poured into the equipment shown, respectively, the condensation reaction was carried out to other reagents, the fluorescence which irradiates ultraviolet rays and is generated in a resultant was measured, and the relation between potassium-cyanide concentration and detection

area was investigated. a result -- drawing 4 as being shown -- it is -- the case of river water -- about [ the case of distilled water, and ] -- it was checked in cyanogen alternative and that it can detect to high sensitivity, without receiving interference by other matter which the response value done one is acquired, therefore is dissolved in the sample solution also about actual sample solutions, such as river water, according to this invention.

[0019]

[Effect of the Invention] according to this invention -- FIA a system -- a gaseous diffusion unit -- a nest -- and -- OPA the cyanides contained by the case in river water etc. as a result of adopting the fluorescence detecting method -- very -- quickness, high sensitivity, and good repeatability -- with -- \*\*\* -- it can detect and, moreover, quantitative measurement can be performed.

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] It is the sketch of the cyanogen detection equipment by this invention.

[Drawing 2] Drawing 1 It is drawing showing the detection peak of the cyanogen obtained when the potassium-cyanide solution from which concentration differs with the equipment shown was measured.

[Drawing 3] Drawing 1 Equipment shown Zero to 100 ng/ml It is drawing showing the relation of the potassium-cyanide concentration and detection area which were obtained when a potassium-cyanide solution was measured.

[Drawing 4] Drawing 1 It sets to a cyanogen addition trial with the equipment shown, and they are river water and distilled water. Zero to 100 ng/ml It is drawing showing the relation of the potassium-cyanide concentration and detection area which were obtained when a potassium cyanide was added and measured.

### [Description of Notations]

R1 : Glycine solution (\*\* 1 class ammonium solution)

R2 : OPA Mixed liquor of a solution and a phosphate buffer

R3 : Phosphate buffer

P : Peristalsis nature pump

S : Sample solution

V : Sample injector

M : Mixed coil

G : Permeability unit

T : Thermostat

RC : Reaction coil

D : Fluorescence detector

R : Addition recorder

W : Waste fluid

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[Translation done.]